

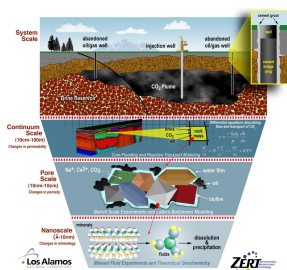
Stability, Reactivity, and Crystal Structure of Na-K Dawsonite

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Acknowledgements:

We thank Dale Counce, Melissa Fittipaldo, and John Kaszuba of Los Alamos for their technical help and expertise. Funding provided by Los Alamos LDRD-DR "Science of Geological Carbon Sequestration". LANL publication LA-UR-05-2846.

Introduction

Dawsonite, $\text{NaAlCO}_3(\text{OH})_2$, is a relatively rare mineral that may play an important role in the geologic sequestration of CO_2 . Numerical calculations such as those of Johnson et al. (2001) consistently show that dawsonite is a likely precipitation product as CO_2 -saturated fluids react with reservoir and cap-rock mineralogy. Dawsonite is also commonly predicted as a supersaturated product in experimental studies. However, dawsonite is rare in nature with reported occurrences numbering in the 10's of localities. In this study, we've examined the kinetics of dawsonite precipitation from several aluminum-bearing precursors and studied phase relations between dawsonite and its K-analog.

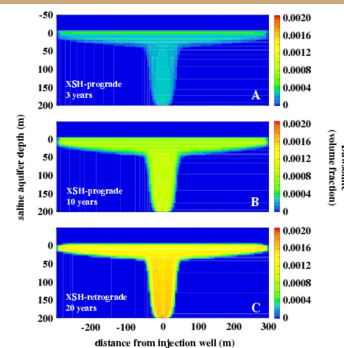


Figure 13: Evolution of Dawsonite ($\text{NaAlCO}_3(\text{OH})_2$) precipitation in model XSH during prograde (3 and 10 years) and retrograde (20 years) sequestration.

Figure from Johnson et al. (2001)

Geochemical Stability of Dawsonite

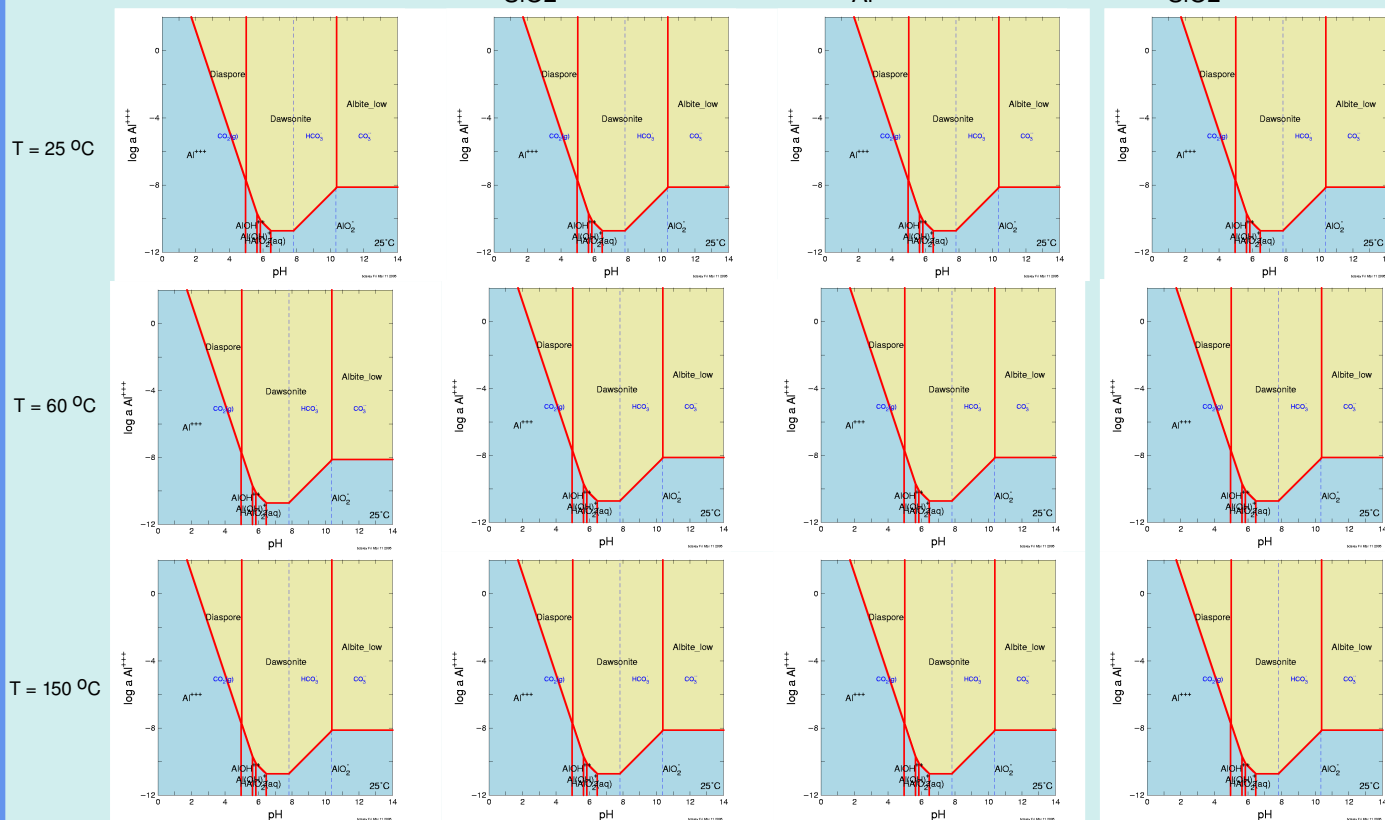
Dawsonite requires a source of Na (or K), Al, and CO_2 . The geological sequestration environment is likely to contain adequate Na (brine) and CO_2 . The main limiting factor then is the availability of Al and the relative stability of dawsonite compared to other Al-bearing minerals. Interestingly, as shown in the diagrams below (calculated with Geochemist's Workbench), silica activity is also important in relation to other key Al-bearing minerals (kaolinite, albite, etc.)

$$\begin{aligned} a_{\text{HCO}_3} &= 1 \\ a_{\text{Na}} &= 1 \\ a_{\text{SiO}_2} &= \text{Quartz} \end{aligned}$$

$$\begin{aligned} a_{\text{HCO}_3} &= 1 \\ a_{\text{Al}} &= 10^{-5} \\ a_{\text{SiO}_2} &= \text{Quartz} \end{aligned}$$

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$$\begin{aligned} a_{\text{Al}} &= 10^{-5} \\ a_{\text{Na}} &= 1 \\ a_{\text{SiO}_2} &= \text{Quartz} \end{aligned}$$



Geochemical Conclusions

Dawsonite has a wide stability field as reflected in numerical studies of geological sequestration.

Dawsonite stability decreases with increasing temperature.

Dawsonite stability is bounded at low pH by clay minerals or Al-hydroxides and at high pH by albite.

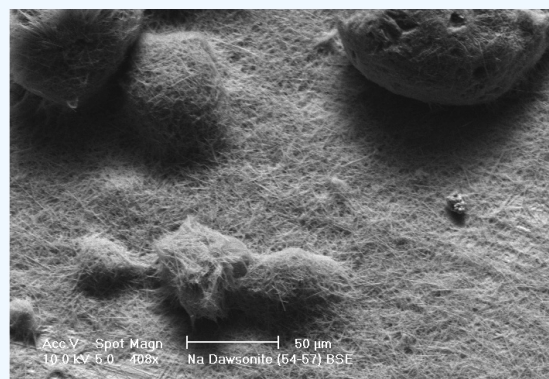
Dawsonite stability is limited at high-silica activities by albite.

Dawsonite may form metastably in the albite field from clay minerals.

Synthesis of Na- and K-Dawsonite

A synthesis method was developed following Zhang et al. (2004) which was optimized to yield well crystallized dawsonite. The syntheses were conducted in sealed Parr vessels (unstirred) containing NaHCO_3 , NaCO_3 , NaOH , and/or NaCl (or the K-equivalents), $\text{Al}(\text{OH})_3$ as analytical-grade gibbsite, and de-ionized H_2O . We investigated the effect of Na/Al ratio, ionic strength, temperature, and time on the rate and extent of dawsonite precipitation.

Dawsonite forms rapidly at 150°C with the reaction complete (all of the gibbsite consumed) within 24 hours. The optimal conditions were Na/Al = 8 in a concentrated NaHCO_3 solution (e.g., 15 g H_2O , 6.8 g NaHCO_3 , 0.78 g $\text{Al}(\text{OH})_3$). Higher pH or lower ionic strength led to lower yields of dawsonite.



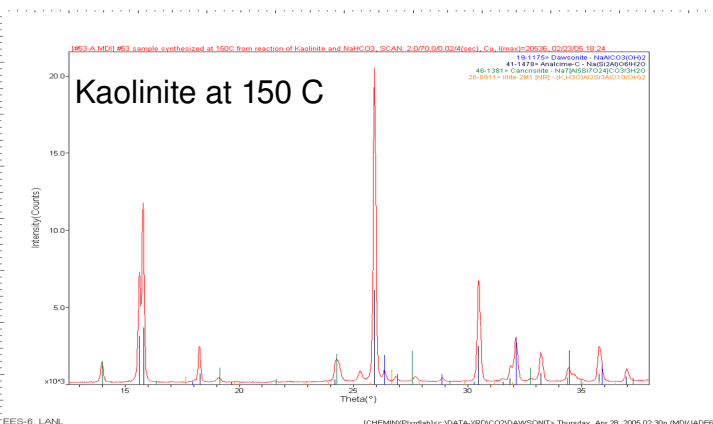
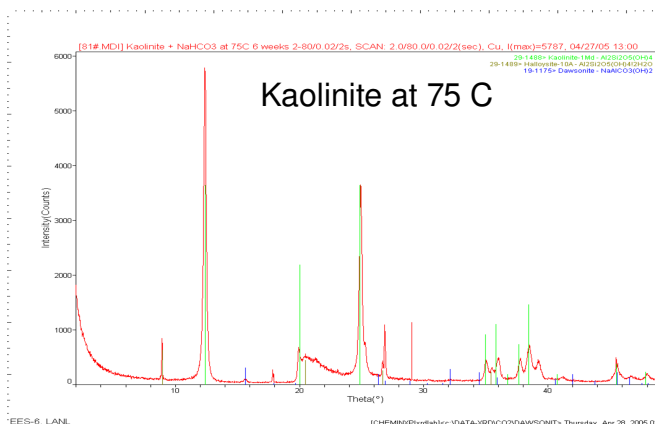
Precipitation of Dawsonite from Al-Minerals in NaHCO₃ Solutions

To investigate the kinetics of dawsonite formation from Al-bearing minerals, we conducted synthesis experiments using a variety of reactive materials. The experiments were done in unstirred Parr pressure vessels using the optimized dawsonite synthesis conditions (Na/Al = 8, concentrated NaHCO₃ solutions) at temperatures ranging from 75 to 200 °C and for times up to 3 months. Our observations include the following:

Albite, montmorillonite, and clinoptilolite do not produce dawsonite but react to form analcime, which appears stable in NaHCO₃ solutions. Kaolinite reacts readily to form dawsonite + analcime at temperatures

as low as 75 °C. Gibbsite reacts completely to dawsonite. However, the addition of quartz to the gibbsite synthesis produced analcime + dawsonite, reducing the yield of dawsonite. The addition of opal-CT had the paradoxical effect of stabilizing gibbsite so that a substantial quantity remained after 4 weeks. Thus, as indicated by the geochemical modeling, high silica activities appear to limit the stability range or at least the rate of formation of dawsonite.

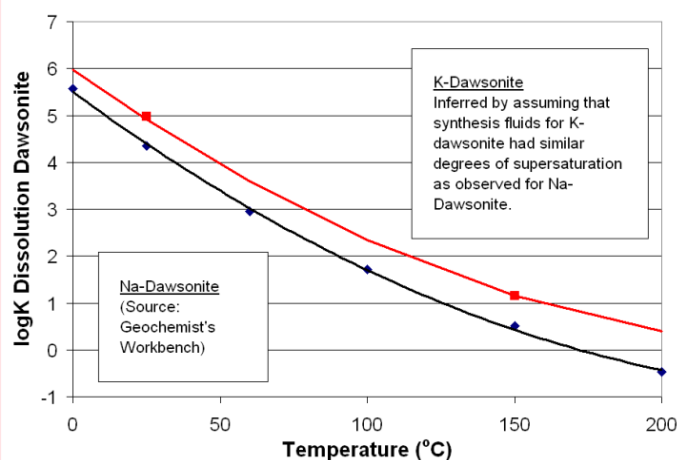
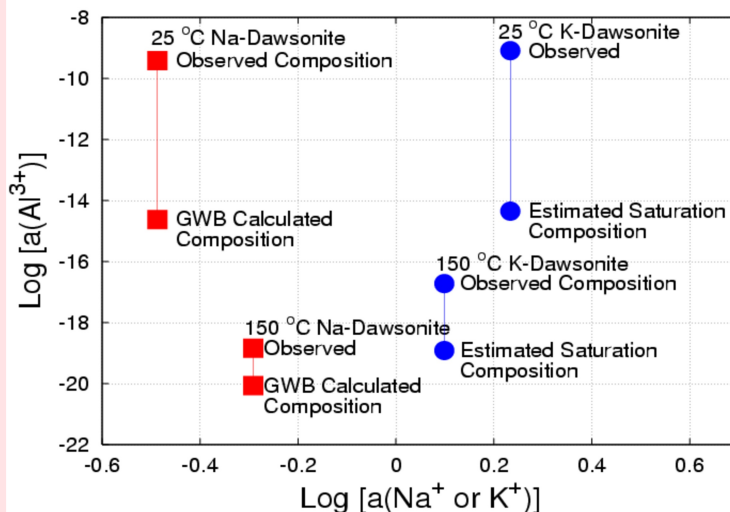
Reactant	75 °C	150 °C	200 °C
Gibbsite	Dawsonite (partial after 40 d)	Dawsonite (complete in 24 hrs)	Dawsonite (complete in 24 hrs)
Gibbsite + Quartz		Dawsonite + Analcime (after 28 days)	
Gibbsite + Opal-CT		Dawsonite (partial after 28 days)	
Kaolinite	Minor Dawsonite (after 40 days)	Analcime + Dawsonite (after 3 months)	Cancrisilite + Dawsonite (after 66 days)
Montmorillonite			Analcime (after 66 days)
Clinoptilolite			Analcime (after 66 days)
Analcime		No Reaction (28 days)	
Albite	No Reaction (after 40 days)	Minor Analcime (after 3 months)	Significant Analcime (after 66 days)



Estimating Thermodynamic Properties of K-Dawsonite

Analysis of supernatant fluids from synthesis experiments suggests that the solubility of K-dawsonite is greater than Na-dawsonite. For example, Al was present at 1.5 ppm in the Na-dawsonite supernatant and 8.1 ppm in the K-dawsonite supernatant. As a method of making these observations semi-

quantitative, an estimate of the solubility product for K-dawsonite was developed. We used Geochemist's Workbench to calculate the saturation state of Na-dawsonite in the Na-dawsonite supernatant at 25 and 150 °C, which provided $\log(Q/K)$ values of 5.2 and 1.2, respectively. We assumed that the supernatant for K-dawsonite was similarly supersaturated. Using Geochemist's Workbench, we speciated the K-dawsonite supernatant and then calculated a solubility product for K-dawsonite using the supersaturation values of Na-Dawsonite. We further assumed that the temperature dependence of the solubility of K-dawsonite was similar to Na-dawsonite. We have used the estimated solubility product of K-dawsonite to evaluate our experimental data and in studies of the potential significance of K-dawsonite in geological sequestration.



Crystal Structure of K-Dawsonite

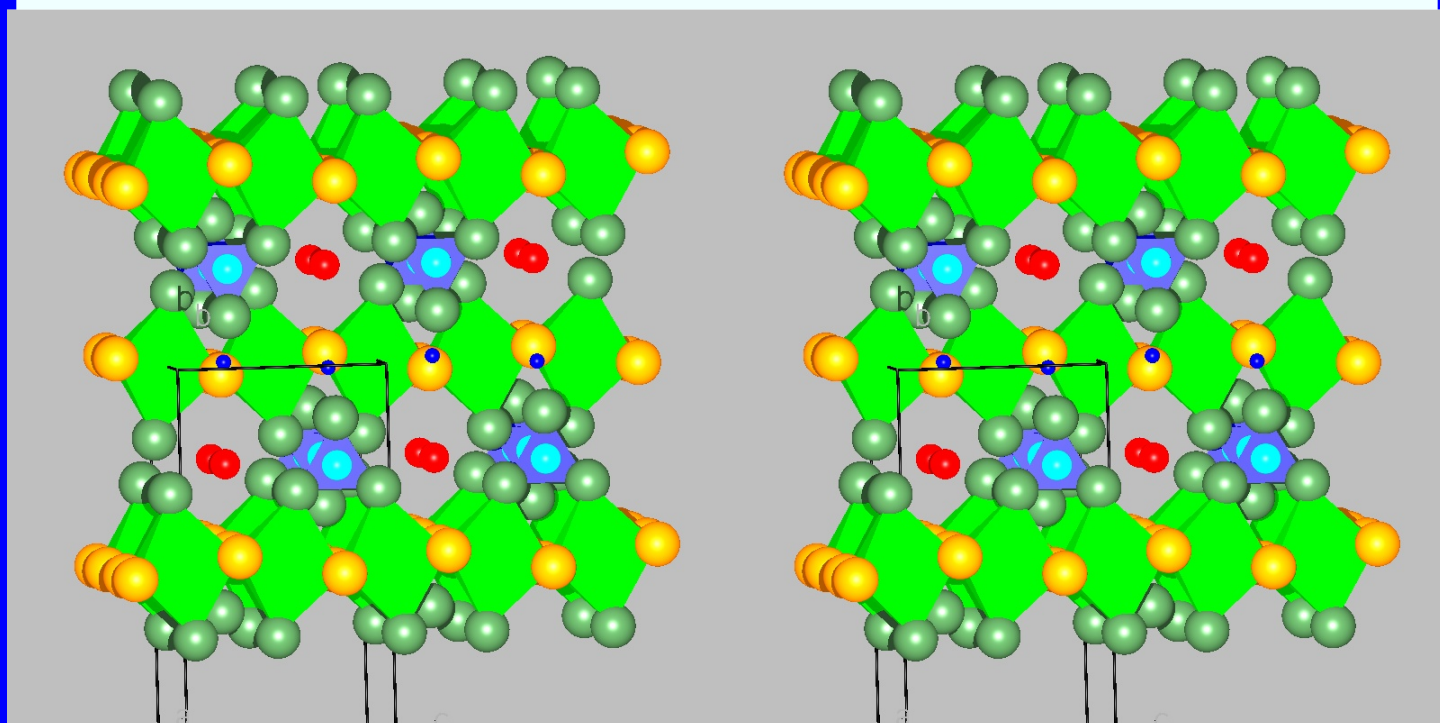
	Space-group	Cell parameter			Density g/cm ³	Volume of cell Å ³
		a	b	c		
K	Cmcm	6.2842	11.9371	5.6287	2.488	422.24
Na	Imma	6.7708	5.5901	10.4415	2.421	395.205

Our synthesis studies showed that K-dawsonite has a crystal structure distinct from Na-dawsonite. The structure of Na-dawsonite (Imma) and NH₄-dawsonite (Cmcm) are known, but the structure of K-dawsonite has not been published*. We used Rietveld analysis to solve the structure of K-dawsonite.

K-dawsonite crystallizes in the Cmcm spacegroup and is a polymorph of NH₄-dawsonite. The structure is similar to Na-dawsonite with chains of Al-octahedra that are cross-linked by carbonate groups and alkali ions. In Na-dawsonite, the carbonate groups and Na-atoms alternate positions giving rise to channels that hold the Na atoms. In K-dawsonite, the carbonate groups and K atoms alternate along the channels.

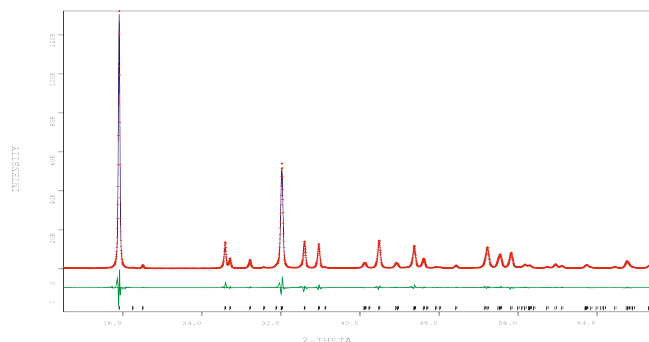
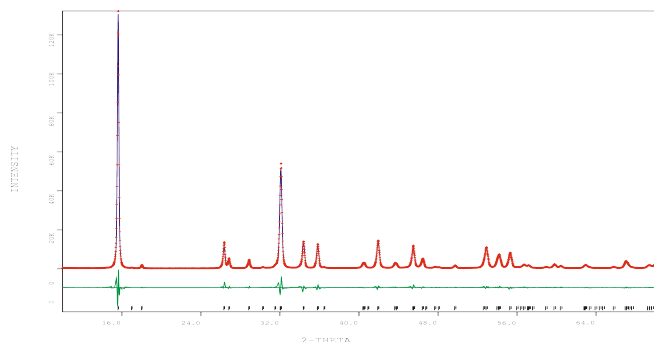
Na-Dawsonite

K-Dawsonite



Na-Dawsonite

Na-Dawsonite



*Following completion of our crystal structure studies, Fernandez-Carrasco (2005) published a structure for K-dawsonite. Our results are in agreement with the newly published data.